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Screening of Novel Catalyst for the Selective Oxidation of Methanol to Formaldehyde

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1. Introduction

Formaldehyde (CH₂O) is produced industrially by the Formox process (CH₃OH + ½O₂ → CH₂O + H₂O) over a ferric molybdate catalyst with a yield of up to 95 % [1]. During the last couple of decades, the methanol feed concentration has steadily increased [1], which has resulted in a catalyst lifetime of only 1-2 years due to volatilization and migration of the active component (molybdenum) leading to an increasing pressure drop over the reactor and loss of selectivity [2,3]. Due to these difficulties, it is of interest to investigate alternative catalyst systems for the oxidation of methanol to formaldehyde.

2. Experimental

Various catalyst systems have been prepared by methods such as impregnation, co-precipitation, citric acid-based sol-gel method and a reflux procedure. The samples were characterized by XRD and BET. The catalysts were tested in a fixed bed reactor with catalyst loadings of 10-50 mg. The feed flow consists of 15 SmL of O₂, 127.5 SmL of N₂ and methanol added through a bubble flask at 6 °C leading to a methanol feed concentration of 3.5-5%. Measurements were performed at app. 250 °C, 300 °C, 350 °C and 400 °C. Experiments with longer time on stream was done for some samples to investigate their stability. The effluent gas was analyzed using a gas chromatograph.

3. Results and discussion

Figure 1 shows the DME corrected selectivity (DME is considered as two methanol when calculating selectivity) for the catalysts containing molybdenum together with results for an industrial iron-molybdate catalyst. In Figure 2 it is shown for vanadium containing systems. It can be seen from both Figure 1 and Figure 2 that catalysts with high selectivities at low conversions have been found. Especially the 25.8 wt% MoO₃ supported on hydroxyapatite (HAP) is interesting, since it performs better than the industrial catalyst at conversions below 80% (temperatures below 350 °C). It can also be seen that some of the vanadium containing catalysts have better DME corrected selectivity than the industrial catalyst at low conversion (low temperature). However, the selectivities at higher conversions for the vanadium based catalyst are generally not as high as for the molybdenum based catalysts. In most cases the vanadium catalysts have higher activity than the molybdenum based catalysts. This is also the case for the vanadium oxide (3 or 5 wt%) on hydroxyapatite catalysts. However, the main problem for the ferric molybdate catalyst is not selectivity and activity, but stability. This will be further investigated for the catalyst with activity and selectivity similar to the industrial catalyst.

4. Conclusions

A range of different Mo and V-based catalysts have been synthesized and tested for selective oxidation of methanol to formaldehyde. In general, the Mo-based catalysts are more selective than the V-based catalysts. A catalyst with high loading of molybdenum oxide on hydroxyapatite seems the most promising with activity and selectivity similar to an industrial iron molybdate catalyst.

References

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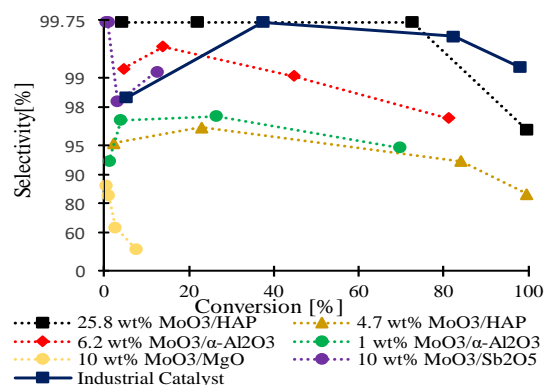


Figure 1. DME corrected selectivity to formaldehyde for molybdenum containing catalysts as function of conversion obtained at temperatures 250, 300, 350 and 400 °C.

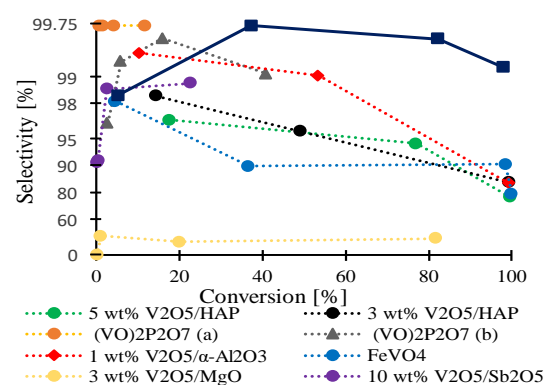


Figure 2. DME corrected selectivity to formaldehyde of vanadium containing catalysts as function of conversion obtained at temperatures 250, 300, 350 and 400 °C.